Collisional vibrational quenching of $NO^+(v)$ ions

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Vibrational quenching rate constants have been measured for $NO^+(v>0)$ ions with 15 neutral quenching molecules by the SIFDT-monitor ion technique. The temperature dependence of the quenching rate constants for the reactions of the neutrals N_2, CO_2, and CH_4 has been investigated from 208 to 450 K. The dependence of the CH_4 quenching rate constant on collision energy has been determined in the energy range 0.03–0.12 eV at 208 and 296 K. Also measured are rate constants for some of the reactions pertinent to the monitor ion technique.

I. INTRODUCTION

Vibrational relaxation of ions in collision with neutrals has only recently begun to be studied, whereas vibrational relaxation of neutral molecules has been investigated over the past several decades. Ion vibrational relaxation experiments have been reviewed by Federer *et al.*[1] The most extensive investigations have employed[1–3] a recently developed[3,4] experimental technique, the monitor ion method, which involves the use of the selected ion flow-drift tube (SIFDT).

The dependence of many ion–molecule reaction rate constants on ion kinetic energy is known to vary with the choice of buffer gas. This is mainly due to rate enhancement caused by the higher ion vibrational temperature with increasing buffer gas mass.[5] The ion vibrational temperature in flow-drift tubes can deviate significantly from the translational temperature of the ions. For this reason, kinetic energy dependences of rate constants for molecular ion reactions measured in flow-drift tubes often cannot be equated with true thermal temperature dependences. This relatively slow rate of equilibration of vibrational temperature with that of translation in flow-drift tubes can be exploited, allowing some investigation of state-to-state kinetics. Absolute rate constants for relaxation of the vibrationally excited ions can be obtained, yielding some information on the nature of the reaction mechanism and on the interaction potential between reacting species.

The collisional quenching of $NO^+(v)$ is of particular interest because of its importance in the earth's ionosphere and in other plasmas involving atmospheric species. While much work has been done on the quenching of $NO^+(v>0)$ by a variety of gases as a function of ion kinetic energy,[1,4] no studies of the temperature dependence of the quenching reactions have been carried out. We investigated the temperature dependences of several of these reactions as a test of the reaction mechanism. In the course of this work we found discrepancies with previous measurements. The present work extends the number of neutral quenching species studied for $NO^+(v>0)$ and provides additional data on the energy dependence for the quenching by methane.

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II. EXPERIMENTAL

The experimental measurements were performed using the variable temperature SIFDT (selected ion flow-drift tube) apparatus which has been described elsewhere.[6] $NO^+(v>0)$ ions were detected by means of the monitor ion method[7] which has been employed[2–4,8,9] in SIFDT experiments in other laboratories to measure rate constants for collisional quenching of vibrationally excited ions by neutrals. A diagram of the present apparatus is shown in Fig. 1. NO^+ ions were produced from NO in a moderate pressure (0.1–1 Torr) electron impact ion source. The ions were mass selected in a quadrupole mass filter and then injected through a Venturi inlet into a fast flow of helium carrier gas ($\sim 10^4$ cm/s at 0.42 Torr). The NO^+ ions were injected with 72 eV of kinetic energy in the laboratory reference frame, enabling vibrational excitation in the injection process (in contrast with the earlier SIFDT studies in which the vibrationally excited ions were formed directly in low pressure sources). Neutral quenching gases were added downstream of the injector.

The $NO^+(v>0)$ ions were detected at the end of the flow tube by means of the monitor ion method in which a monitor gas, in this case CH_3I, was added ~ 1 cm upstream of the sampling aperture of a second (downstream) mass spectrometer. Since the ionization potential of CH_3I (9.53 eV)[10] is greater than the recombination energy of NO^+ (9.265 eV),[10] charge transfer from $NO^+(v=0)$ to CH_3I is endoergic and does not proceed at a significant rate. Charge transfer from $NO^+(v>0)$ to CH_3I is exoergic and proceeds rapidly [the recombination energy of $NO^+(v=1)$ is 9.56 eV[10]]. Therefore, the measured CH_3I^+ signal intensity is proportional to the concentration of $NO^+(v>0)$ ions. $NO^+(v>1)$ ions can be detected similarly by using NO_2 as the monitor gas. Relative vibrational state populations of the NO^+ ions were determined by recording the total NO^+ signal intensity versus the CH_3I gas flow rate (added at the reactant inlet rather than the monitor inlet), shown plotted in Fig. 2. The initial nonlinear decay is due to the excited states $v>0$ reacting more rapidly than the $v=0$ state. The dashed line is the $NO^+(v=0)$ signal extrapolated to zero CH_3I flow rate. The difference between the dashed line and the total NO^+ signal points represents the $NO^+(v>0)$

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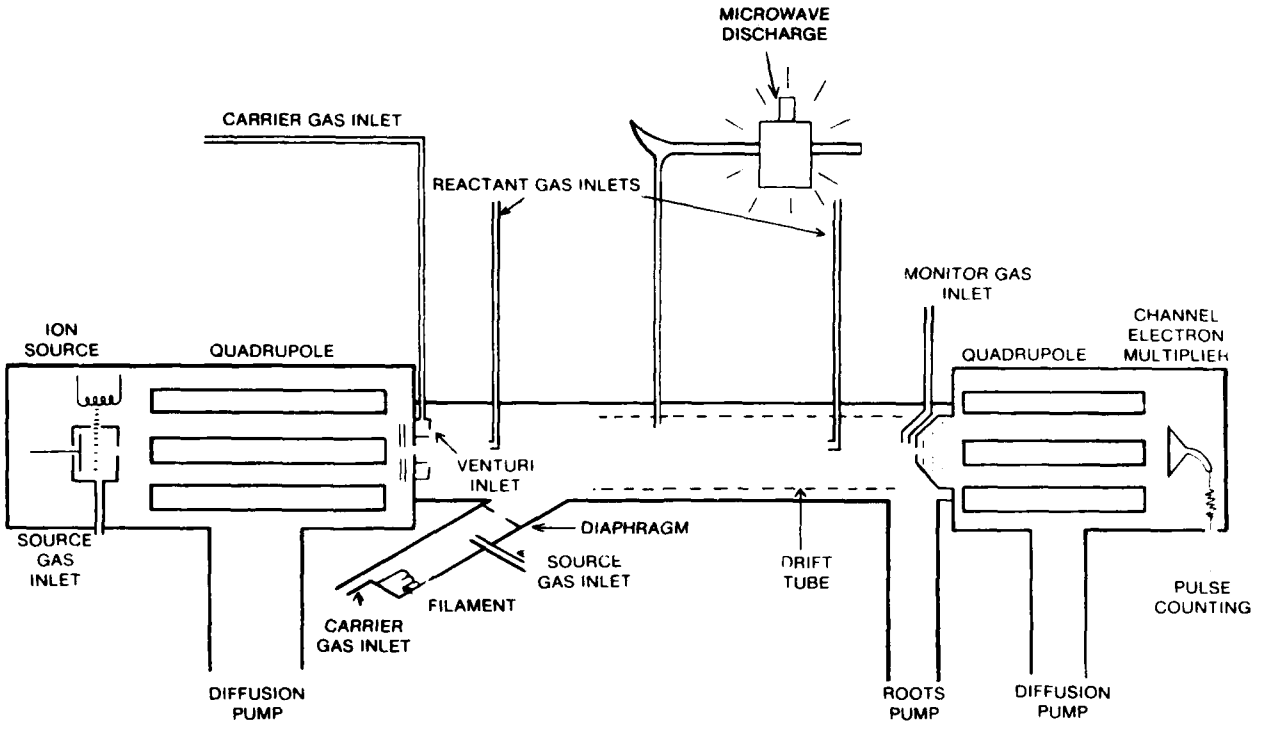

FIG. 1. Schematic diagram of the selected ion flow-drift tube (SIFDT) apparatus at AFGL.

states. This difference is plotted as squares in Fig. 2. The intersections of the solid and dashed lines with the ordinate are, respectively, the relative $NO^+(v>0)$ and $NO^+(v=0)$ concentrations in the absence of CH_3I. This procedure was also followed for the NO_2 monitor gas in order to quantify the $NO^+(v>1)$ population [a rapid rate of charge transfer between $NO^+(v>1)$ and NO_2 was assumed]. These measurements indicated that the relative vibrational populations depend on ion injection energy and that at 100 eV (laboratory frame) injection energy, the total NO^+ signal was composed of 48% $v>0$ and 12% $v>1$ states. At 72 eV injection energy, the $v>1$ population was too low to be determined accurately but was less than 10% of the total NO^+, and the $v>0$ states constituted 23% of total NO^+. The possibility of the production of electronically excited $NO^+(a\,^3\Sigma^+)$ was ruled out experimentally by noting the absence of the product N_2^+ of the fast[11,12] reaction $NO^+(a\,^3\Sigma^+) + N_2 \rightarrow N_2^+ + NO + 0.07$ eV ($k = 7\times10^{-10}$ cm^3 s^{-1}).

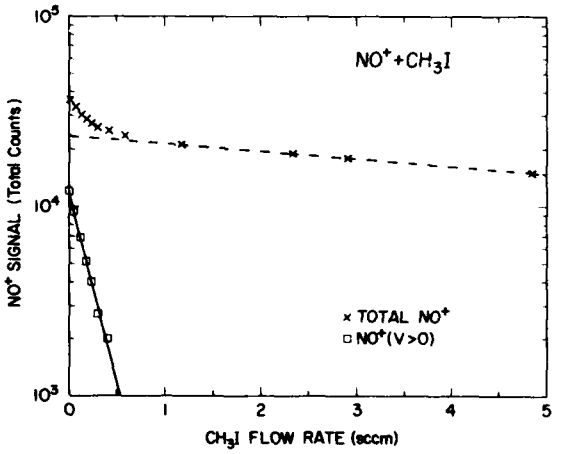

FIG. 2. NO^+ ion signal vs CH_3I gas flow rate. The dotted line represents the $NO^+(v=0)$ signal extrapolated to zero CH_3I flow rate. The $NO^+(v>0)$ points on the solid line were obtained by subtraction of the extrapolated $NO^+(v=0)$ signal from the experimental total NO^+ ion signal points.

For study of the quenching by CH_4, N_2, and CO_2, the temperature was varied by pumping heated oil or chilled methanol through a heat exchanger in contact with the flow tube. The quenching rate constant for CH_4 was measured as a function of ion kinetic energy by varying the electric field in the drift tube section of the SIFDT.

The reactions pertinent to the monitor ion technique were investigated in separate experiments in the SIFDT apparatus using standard methods of flow tube kinetics.[6] The reactions of CH_3I with $NO^+(v=0)$ and $NO^+(v>0)$ were measured by injecting NO^+ ions into the flow tube and recording the NO^+ signal as a function of the CH_3I flow rate, as described above. The solid line shown in Fig. 2 is the difference between the experimental points (total NO^+) and the extrapolated dotted line [$NO^+(v=0)$], giving the decay of the $NO^+(v>0)$ ions, and thus yielding the rate constant for $NO^+(v>0) + CH_3I$. The reaction $CH_3I^+ + CH_3I$ was studied by injecting CH_3I^+ ions (produced by electron impact on CH_3I) and adding CH_3I through the reactant inlet. The rate constant for the reaction $CH_3I^+ + N \rightarrow H_2CN^+ + HI$ was determined by producing N atoms in a microwave discharge in N_2 (see Fig. 1), assuming 1% dissociation of N_2, and reacting the N atoms with injected CH_3I^+. All of the gases used in the experiments were obtained commercially and were used without further

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Vibrational quenching rate constants have been measured for $NO^+(v>0)$ ions with 15 neutral quenching molecules by the SIFDT-monitor ion technique. The temperature dependence of the quenching rate constants for the reactions of the neutrals N_2, CO_2, and CH_4 has been investigated from 208 to 450 K. The dependence of the CH_4 quenching rate constant on collision energy has been determined in the energy range 0.03–0.12 eV at 208 and 296 K. Also measured are rate constants for some of the reactions pertinent to the monitor ion technique.

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purification. The overall uncertainties for all of the rate constants reported are ± 30%.

III. RESULTS

A. Reactions pertinent to the monitor ion method

As was stated previously, charge transfer from $NO^+(v=0)$ to CH_3I is endoergic and does not proceed at a significant rate. However, these species react via association to form $(NOCH_3I)^+$. The rate constant for this reaction was measured at 0.42 Torr and 298 K and is equal to 3.9×10^{-11} $cm^3\,s^{-1}$. The reaction $NO^+(v>0) + CH_3I \rightarrow NO + CH_3I^+$ is exoergic and proceeds rapidly with a rate constant of 1.9×10^{-9} $cm^3\,s^{-1}$. A plot of the experimental data is shown in Fig. 2. A knowledge of the rate constant for $NO^+(v>0) + CH_3I$ was required in order to ensure that the reaction rate is sufficiently rapid for this reaction to be used as a monitor of $NO^+(v>0)$ in the quenching experiments.

The reaction between CH_3I^+ and its parent neutral was investigated due to the possible role of this reaction in the monitor ion detection scheme. The rate constant for this reaction at 0.42 Torr and 298 K was determined to be 1.5×10^{-10} $cm^3\,s^{-1}$. No products of the reaction were detected below mass 200, the upper mass limit of the downstream (detection) mass spectrometer. However, Sieck and Gorden[13] have found the major product of this reaction to be the association product $(CH_3I)_2^+$ at pressures above 0.01 Torr and have measured a rate constant of 1.2×10^{-11} $cm\,s^{-1}$ over the pressure range 5×10^{-4} to 0.1 Torr. Other reported values for this rate constant are 2.4×10^{-11} $cm^3\,s^{-1}$ in the range 0.001 to 0.2 Torr[14] and 5.5×10^{-12} $cm^3\,s^{-1}$ from 10^{-7} to 10^{-3} Torr.[15] The higher value of our rate constant compared with these is attributed to significant three-body reaction under our higher pressure conditions. The fact that CH_3I^+ reacts with CH_3I indicates that in monitoring the $NO^+(v>0)$, it is possible to add too much CH_3I, and that appropriate precautions should be taken.

The rate constant for CH_3I^+ with N was also measured. Assuming 1% dissociation of N_2 in the microwave discharge,[16] the rate constant for CH_3I^+ reacting with N to form $H_2CN^+ + HI$ is 5×10^{-11} $cm^3\,s^{-1}$. This reaction is important in the study of vibrational energy transfer from $N_2(v=1)$ to $NO^+(v=0)$.

B. Collision quenching of $NO^+(v>0)$

Rate constants k_q for collisional vibrational quenching of $NO^+(v>0)$ by 15 neutral quenching gases measured at thermal energy at 296 K are presented in Table I. Also tabulated are the Langevin limiting values of the collision rate constants k_c (calculated incuding the dipole interaction for the polar neutrals by the method given in Ref. 17). The variation of the $NO^+(v>0)$ quenching rate constants with temperature for the neutrals N_2, CO_2, and CH_4 is shown in Fig. 3. A plot of k_q vs center-of-mass kinetic energy for the $NO^+(v>0) + CH_4$ collision is given in Fig. 4 for two experimental temperatures 208 and 296 K. The thermal energy rate constant measured at 450 K is also included in the figure.

IV. DISCUSSION

A. Collisional quenching of $NO^+(v>0)$ at thermal energy, 296 K

1. Neutrals studied previously: Kr, Xe, N_2, O_2, CO, CO_2, NO_2, and CH_4

Vibrational quenching of $NO^+(v>0)$ by the neutrals Kr, Xe, N_2, O_2, CO, CO_2, NO_2, and CH_4 has been investigated by Federer *et al.*,[1] and the rate constants have been included in Table I for comparison. The present results agree with those of the Innsbruck group[1] to within a factor of 3 for N_2

TABLE I. Measured quenching rate constants k_q for the collisional vibrational quenching of $NO^+(v>0)$ by various neutrals at thermal collision energy. Also given are the ion–neutral collision rate constants k_c, the number of collisions Z required for quenching, the neutral polarizabilities α, the quantities $(\epsilon_{mm}/k)^{1/2}$ where ϵ_{mm} is the neutral–neutral well depth (see text), the quenching rate constants $k_{Innsbruck}$ measured in Innsbruck,[a] and the ratio of the quenching rate constant for $O_2^+(v=1)$[b] (where available) to k_q.

Neutral	k_q ($cm^3\,s^{-1}$)	k_c ($cm^3\,s^{-1}$)	Z ($=k_c/k_q$)	α (Å^3)	$(\epsilon_{mm}/k)^{1/2}$ (K$^{1/2}$)	$k_{Innsbruck}$ ($cm^3\,s^{-1}$)	$k_q(O_2^+)/k_q$
Kr	< 1(−13)	7.8(−10)	> 7800	2.48	13.1	< 1(−12)	> 110
Xe	2.8(−13)	9.5(−10)	3400	4.04	14.9	< 1(−12)	
N_2	2.6(−12)	8.1(−10)	310	1.74	9.7	7(−12)	0.73
O_2	< 3(−13)	7.5(−10)	> 2500	1.58	10.8	< 1(−12)	> 1000
CO	4.9(−12)	8.9(−10)	180	1.95	10.2	1(−11)	9.0
CO_2	1.1(−10)	9.5(−10)	8.6	2.91	14.0	4(−11)	0.91
NO_2	8.3(−11)	1.05(−9)	13	3.02	18.4	1.5(−10)	
SO_2	6.1(−11)	2.0(−9)	33	4.00	17.9		9.3
CH_4	5.0(−11)	1.2(−9)	24	2.59	12.1	3(−11)	12.0
CH_3F	1.7(−10)	2.4(−9)	14	2.97	16.4		
CH_3Cl	5.7(−10)	2.4(−9)	4.2	4.72	19.8		
CH_3Br	6.5(−10)	2.2(−9)	3.4	5.79	20.2		
C_2H_6	6.6(−10)	1.3(−9)	2.0	4.45	15.4		
C_3H_8	1.0(−9)	1.4(−9)	1.4	6.33	15.3		
SF_6	2.2(−12)	1.2(−9)	545	6.54	14.2		50

[a] See Ref. 1.
[b] See Ref. 3.

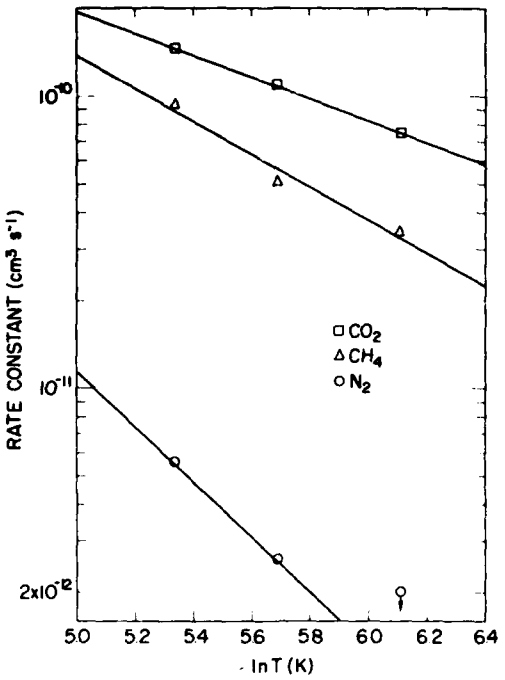

FIG. 3. Rate constants for vibrational quenching of $NO^+(v>0)$ ions by CO_2, CH_4, and N_2 vs the logarithm of absolute temperature. The point with the arrow denotes a rate constant upper limit.

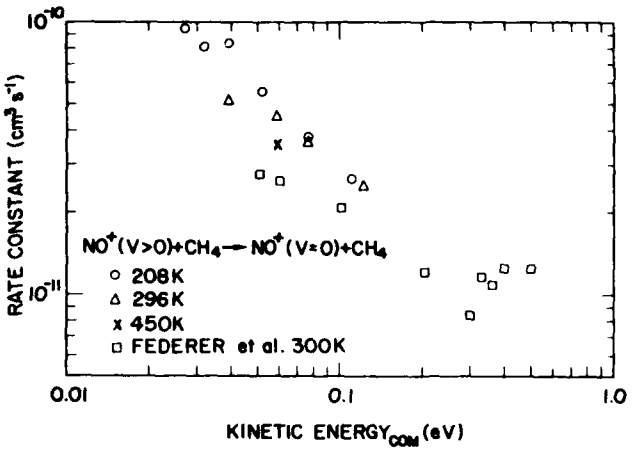

FIG. 4. Rate constants for vibrational quenching of $NO^+(v>0)$ ions by CH_4 vs center-of-mass ion kinetic energy at 208 and 296 K. Included is the rate constant measured at 450 K and zero applied drift field. Also included are the data of Federer *et al.* (Ref. 1).

and CO_2, and to within a factor of 2 for CO, NO_2, and CH_4. There is no obvious evidence of a systematic difference between the two sets of results since the present rate constants are more or less evenly scattered above and below the previous values. However, it was found that several flushings of the reactant inlet system with each neutral quenching gas were required in order to obtain reproducible rate constants. This was especially true for quenchers exhibiting small rate constants, where a slight impurity of a fast quencher might easily affect the measured rate constant. Effects due to impurities are otherwise hard to observe since both the primary and product ions are the same regardless of quencher. This effect may explain some of the differences between the present results and those of the Innsbruck group.[1]

In the cases of Kr and O_2, the present work has extended the rate constant upper limits to lower values, and for Xe, the rate constant has been established to be 2.8×10^{-13} cm^3 s^{-1}.

There is a cogent body of evidence indicating that long range forces of attraction are generally responsible for the efficient relaxation of vibrationally excited ions in collision with neutrals.[18] In a model developed by Dobler *et al.*[4] and Ferguson,[19,20] the observed vibrational quenching of $NO^+(v>0)$ is attributed to a V→T transfer mechanism involving complex formation followed by vibrational predissociation, and is discussed in detail in the above references. The mechanism may actually involve transfer of ion vibrational energy into translation plus a lower frequency vibration of the neutral.[1] The model also predicts some rotational excitation of the products.[20] While it is believed that quenching proceeds via this collision complex mechanism for most of the neutrals in this study, the possibility of a direct mechanism involving nearly resonant V→V energy transfer to a fundamental vibrational mode of the quenching molecule was considered for each neutral. For the polyatomic quenchers, there is also the possibility of near-resonant V→V transfer to the numerous vibrational overtone modes.

For N_2 and CO, it is unlikely that the nearly resonant V→V transfers are responsible for vibrational quenching of $NO^+(v>0)$.[1] This was shown[21] for N_2 by a detailed balance argument when no detectable reverse reaction could be observed. For CO, quenching rate enhancement by V→V transfer is improbable in view of the larger quenching rate constant for O_2^+ quenched by CO than that for NO^+ quenched by CO, the former having the greater energy defect for resonant V→V transfer. In the case of CO_2 however, quenching by the nearly resonant (energy defect = 5 cm^{-1}) V→V transfer cannot be ruled out. In general,[1] vibrational quenching rate constants for O_2^+ are greater than those for NO^+. Table I gives the ratio of the quenching rate constant for O_2^+ to that of NO^+ for the cases where both have been measured. The rate constant for $NO^+(v>0)$ quenching by CO_2 measured in our laboratory is nearly identical to the published value for quenching of $O_2^+(v>0)$ by CO_2, and it is therefore possible that the rate for quenching of NO^+ by CO_2 is enhanced by nearly resonant V→V energy transfer. For O_2, NO_2, and CH_4, there are no near-resonant V→V transfer possibilities. The low value of the quenching rate constant for O_2 may be due to a repulsive interaction between $O_2(^3\Sigma)$ and $NO^+(^1\Sigma)$[1]. Vibrational quenching of $NO^+(v>0)$ by all of the above species is discussed in detail by Federer *et al.*[1]

2. CH_3F, CH_3Cl, and CH_3Br

There exist no opportunities for nearly resonant V→V transfer to the fundamental vibrational modes of the quenchers CH_3F, CH_3Cl, and CH_3Br. Quenching by these species occurs with high efficiency, as is generally true for polar neutrals. Federer *et al.*[1] introduced the idea of correlating quenching rate constants for the $NO^+(v>0)$ ion with

the quantity $(\epsilon_{mm}/k)^{1/2}$ where ϵ_{mm} is the neutral–neutral well depth (ϵ_{mm} values are tabulated by Lin *et al.*[22]) and k is Boltzmann's constant. The treatment is based on the assumption of a combination relationship where the ion–neutral well depth $\epsilon_{NO^+\cdot M}$ is proportional to $(\epsilon_{NO^+\cdot NO^+}\cdot\epsilon_{mm})^{1/2}$ where $\epsilon_{NO^+\cdot NO^+}$ and ϵ_{mm} are the ion–ion and neutral–neutral well depths, respectively. For comparison of relative interaction energies in the series $NO^+\cdot M$, such ion–neutral interaction potentials might be expected to vary in proportion to the relative values of $\epsilon_{mm}^{1/2}$. Actual interaction potentials for $NO^+\cdot M$ are not available for most of the neutrals studied.

The quenching probabilities $1/Z$ are plotted vs $(\epsilon_{mm}/k)^{1/2}$ in Fig. 5. It can be seen that there is good correlation for the halomethane series CH_3F, CH_3Cl, CH_3Br, suggesting that the magnitudes of the quenching rate constants for this series are governed by the strength of the ion–neutral interaction. This provides some support for the model of complex formation followed by vibrational predissociation. Some additional support for the model may be seen in Fig. 6, which is a plot of the quenching probability for the reactions studied vs neutral polarizability. A rough correlation is evident for the series CH_4, CH_3F, CH_3Cl, CH_3Br.

3. C_2H_6 and C_3H_8

Ethane and propane also have no opportunities to quench $NO^+(v>0)$ by near-resonant $V\rightarrow V$ transfer to fundamental vibrational modes. However, the large number of vibrational overtone modes for these species invites the possibility for $V\rightarrow V$ transfer to these modes. The quenching by these molecules is very efficient, as expected from their large polarizabilities. In Fig. 6, a rough correlation between quenching probability and neutral polarizability can be seen for the series CH_4, C_2H_6, C_3H_8.

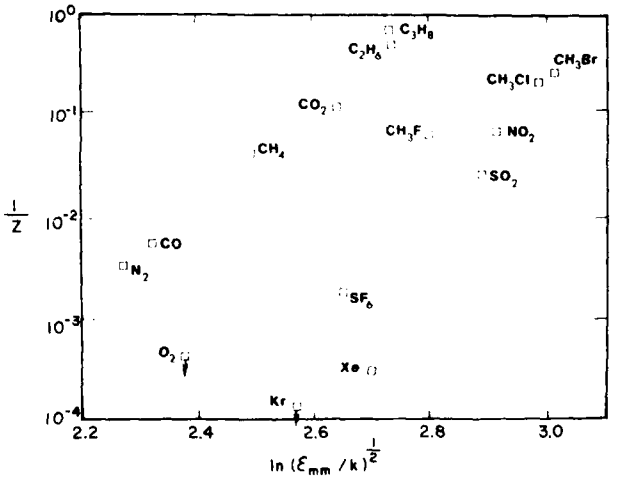

FIG. 5. Vibrational quenching probability ($1/Z$) for the quenching gases vs the logarithm of $(\epsilon_{mm}/k)^{1/2}$ where ϵ_{mm} is the neutral–neutral potential well depth and k is Boltzmann's constant. Points with arrows denote quenching probability upper limits.

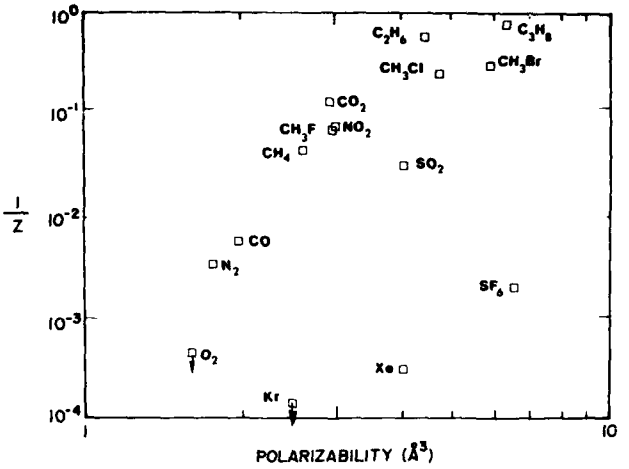

FIG. 6. Vibrational quenching probability ($1/Z$) for the quenching gases vs quenching gas polarizability. Points with arrows denote quenching probability upper limits.

4. SO_2 and SF_6

There are no nearly resonant $V\rightarrow V$ possibilities (fundamental modes) for SO_2 or for SF_6. In the case of SF_6, the quenching of O_2^+ is 50 times faster[3] than the quenching of NO^+. The NO^+ quenching probability for SF_6 seems anomalously low given the relatively high polarizability of SF_6. This point is illustrated in Fig. 6. In addition, Fig. 5 shows that the large value of the SF_6–SF_6 well depth does not correspond to a high probability for quenching. A possible explanation for the low value of k_q for the SF_6/NO^+ system compared with that of SF_6/O_2^+ is offered in the fact that the charge distribution in $NO^+(^1\Sigma)$ is isotropic in nature, which could lead to a weaker interaction than that between SF_6, which has an isotropic polarizability, and the anisotropic O_2^+. Anisotropy of the interaction potential between the ion and the quenching species has been postulated[20] as a likely requirement for efficient vibrational relaxation.

B. Temperature dependence of k_q for N_2, CO_2, and CH_4

Expressions for the temperature dependences of the $NO^+(v>0)$ quenching rate constants for the neutrals N_2, CO_2, and CH_4 are presented in Table II. The observed trend shows decreasing quenching rate constants with increasing temperature, which is generally consistent with the kinetic

TABLE II. Expressions for the temperature dependence of the quenching rate constants k_q for the three neutral quenchers N_2, CO_2, and CH_4 obtained by a least squares analysis of the data.

Neutral	Rate constant expression (cm^3s^{-1})
N_2[a]	$k_q = 2.4\times10^{-12}(300/T)^{2.1}$
CO_2	$k_q = 1.1\times10^{-10}(300/T)^{0.87}$
CH_4	$k_q = 5.6\times10^{-11}(300/T)^{1.3}$

[a] Rate constant expression calculated from two experimental points (omitted is the highest temperature point which is an upper limit to k_q; see Fig. 4).

energy dependence results of the Innsbruck study on NO^+.[1]

In accord with the model discussed in Ref. 19 the quenching rate constant can be expressed as follows:

$$k_q = k_c k_{vp}/k_{-1},$$

where k_c is the collision capture rate constant, k_{vp} is the rate constant for vibrational predissociation of the complex, and k_{-1} is the rate constant for unimolecular decomposition of the complex back into reactants. In this expression it is assumed that $k_{-1} \gg k_{vp}$ and that a complex is formed on every collision. Herbst[23] and Bates[24] have modeled the temperature dependence of the ratio k_c/k_{-1} in the form $T^{-l/2}$, where l is the total number of rotational degrees of freedom of the reactants. The magnitudes of the measured negative temperature dependences for CO_2 and CH_4 are less than those expected from the $T^{-l/2}$ type of dependence, suggesting that the rate constants for vibrational predissociation of the complex k_{vp} may have some positive temperature dependence. The temperature dependence of N_2, however, agrees well with that predicted by the theory.

C. Kinetic energy dependence of k_q for CH_4

The dependence of k_q on ion–neutral center-of-mass kinetic energy for CH_4 is shown graphically in Fig. 4. The results from the Innsbruck study are included for comparison. The present results are shifted upward from the Innsbruck results by a factor of approximately 1.6. It can be seen in Fig. 4 that the magnitude of the temperature dependence of the quenching rate constant is significantly greater than that of the energy dependence at zero or low drift field and that the two coincide at higher fields. The fact that the temperature dependence is larger than the energy dependence is not surprising. The theory[23,24] mentioned above would predict an E^{-1} energy dependence, but a $T^{-5/2}$ temperature dependence for this system, the difference being that in an electric field only the internal states of the ion are heated and not those of the CH_4. This effect has been confirmed by recent work on three-body associations by the Birmingham group.[25] The energy dependence at 208 K is $E^{-0.92}$. At 296 K the energy dependence is $E^{-0.62}$ including the low energy point and is the same as the 208 K data excluding the low energy point. The steeper dependence is close to what theory would predict. The temperature dependence of the rate constant for this reaction is approximately half as steep as theory would predict. This indicates that the deviation may arise from effects due to CH_4 rather than NO^+.

D. Rate constants involved in the study of $NO^+(v=0)+N_2(v=1)$

The vibrational energy transfer from $N_2(v=1)$ to $NO^+(v=0)$ has been studied by Ferguson *et al.*,[21] who found that the rate constant for this reaction is smaller than 10^{-13} cm^3 s^{-1}. We have measured several of the rate constants involved in this study and conclude that the limit given by Ferguson *et al.*[21] should be raised to 3×10^{-13} cm^3 s^{-1}. This is based on the following reactions:

$$NO^+(v=1) + CH_3I \rightarrow CH_3I^+ + NO, \quad (1)$$

$$NO^+(v=0) + CH_3I \rightarrow (NOCH_3I)^+, \quad (2)$$

$$CH_3I^+ + CH_3I \rightarrow m/e > 200, \quad (3)$$

$$CH_3I + N \rightarrow H_2CN^+ + HI, \quad (4)$$

$$NO^+(v=1) + N_2 \rightarrow N_2 + NO^+(v=0), \quad (5)$$

$$NO^+(v=1) + N_2(v=0) \rightarrow N_2(v=1) + NO^+(v=0), \quad (6)$$

$$NO^+(v=0) + N_2(v=1) \rightarrow N_2(v=0) + NO^+(v=1). \quad (7)$$

All of these reactions took place in the experiments of Ferguson *et al.*[21] The rate constants for reactions (1)–(5) are given in the results section of this paper. Reaction (6) was postulated to be the quenching mechanism because of (1) the near resonance of the vibrational energy levels between N_2 and NO^+ and (2) the fast quenching rate for reaction (1) compared to the O_2^+ quenching rate. Reaction (7) was the reaction being studied. It is difficult to set the conditions of the experiment such that it is possible to observe the CH_3I^+ product resulting from reaction (7) followed by reaction (1). If too much CH_3I was added, reaction (3) was liable to proceed, and if too little was added reaction (6) dominated reaction (1). Reaction (4) would also seriously deplete the CH_3I^+ signal. Therefore, the sensitivity of the experiment was lowered. Only a decline in the NO^+ signal could be detected rather than an increase in the CH_3I^+ signal. The limit to the rate constant for reaction (1) should therefore be raised slightly to correspond to this decreased sensitivity.

V. CONCLUSIONS

The measured rate constants for quenching of $NO^+(v>0)$ by a variety of neutrals generally scale with neutral polarizability and neutral–neutral well depth, as expected. The main exception is SF_6 for which k_q is anomalously low, possibly reflecting a highly isotropic interaction potential. The temperature dependence results reveal decreasing rate constants with increasing temperature, and the magnitudes of the temperature dependences for CO_2 and CH_4 are smaller than those expected from simple theory. This suggests the possibility of some temperature dependence in the vibrational predissociation rate constant. The rate constants for the quenching of $NO^+(v>0)$ by CH_4 also decrease with increasing energy. This decrease is in line with that expected from theory.

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